CATEGORIZATION
OF
ALUMINUM ALKYLS

Submitted by:
THE ALUMINUM ALKYLS CONSORTIUM

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March 20, 2001
Revised August 23, 2001

High Production Volume Chemicals
Aluminum Alkyls

The Aluminum Alkyls Consortium (AAC) is a group of manufacturers committed to assuring the human and environmental safety of their chemicals. As such a consortium, the AAC has agreed to participate in the US EPA High Production Volume (HPV) Chemicals Challenge Program by sponsoring a group of HPV chemicals and mixtures for study. These chemicals are:

Chemical Name	CAS Number
aluminum triethyl	97-93-8
aluminum chlorodiethyl	96-10-6
aluminum tri isobutyl	100-99-2
aluminum dichloroethyl	563-43-9
aluminum tri n-octyl	1070-00-4
aluminum tributyl	1116-70-7
aluminum trihexyl	1116-73-0
aluminum tri (C2-C20) alkyls	68908-97-4
aluminum trichloro triethyldi	12075-68-2
aluminum diisobutyl chloride	1779-25-5
aluminum tridodecyl *	1529-59-5
aluminum trihexadecyl *	1726-65-4
aluminum tris (decyl) *	1726-66-5
aluminum trioctadecyl *	3041-23-4
aluminum tridocosyl *	6651-25-8
aluminum tritetracosyl *	6651-26-9
aluminum trioctacosyl *	6651-27-0
aluminum trihexacosyl *	10449-71-5
aluminum triethyl *	97-93-8
aluminum tributyl *	1116-70-7
aluminum trihexyl *	1116-73-0
aluminum trioctyl *	1070-00-4
aluminum trieicosyl *	1529-57-3
aluminum tritetradecyl *	1529-58-4

* Components of tri (C2-C20) alkyls, not all have physical/chemical data

AAC believes that these chemicals appropriately belong in a single study group-based category based on the highly reactive nature of the aluminum alkyls i.e., their immediate reaction with both air and water resulting in breakdown of the compounds. Indeed, it does not appear to be meaningful, feasible or safe to perform mammalian or ecotoxicological tests on such a reactive group.

Aluminum alkyls are highly reactive materials that are used in a variety of industrial chemical processes such as polymerization, oligomerization, alkylation, and stereochemical synthesis. They are compatible and miscible in

all proportions with saturated aliphatic and aromatic hydrocarbons such as pentane, hexane, heptane and toluene. They combine rapidly with compounds containing oxygen and are extremely hazardous during such combinations (Wissink, 1997). These reactions may result in ether cleavage accompanied by gas evolution (Mole and Jeffery, 1972).

In a final rule, OSHA established an 8-hour TWA limit of 2 mg/m^3 for both the soluble salts of aluminum and the aluminum alkyls. The agency concluded that these limits will protect against the significant risk of irritation and skin burns which constitute material health impairments that are associated with exposures at levels above the PEL (OSHA, 1988). Although toxicity data are sparse for the aluminum alkyls, it is known that all of the nonhalogenated alkyls may decompose into aluminum oxide fume, and the halogenated alkyls are even more irritating because of acid hydrolysis (ACGIH, 1991).

Structures and Properties

Structures of the aluminum alkyls and the chloroaluminum alkyls discussed in this document are presented in Table 1. These structures are strikingly similar for the alkyl moieties, differing only in length of the alkyl group. The chlorinated compounds are also very similar in structure except for a halide displacement of an alkyl.

Most of the chemistry of organoaluminum compounds can be readily explained in terms of the Lewis acidity of organoaluminum monomers, directly related to the tendency of the aluminum atom to build up an octet of electrons. Reactions of these substances are explosive, particularly for those without halide components. Halogenated compounds may exhibit the same reactivity but at a slower rate (Mole and Jeffrey, 1972). Their Lewis acidity results in self-association of organoaluminum compounds. Halides arise from association of the Lewis acidic aluminum center with a lone pair of electrons from the electronegative atom. The trialkyl aluminums are highly reactive towards oxidizing agents including molecular oxygen, thus, the fast reactions in air. This high reactivity extends to the less strongly associated derivatives such as the dialkylaluminum halides.

Reactivity

Pyrolyis occurs frequently by non-radical mechanisms (Tajima and Marsel). The volatile products of triethylaluminum, for example were found to be ethene, ethane, 1-butene, cis and trans-2-butene, hydrogen and lesser amounts of methane, butane and hexenes (Smith and Wartik). Breakdown products are expected to be long or short chain alkyls or the oxidized components of these. Shorter chain compounds are more reactive species based on the flash points (Table 2); however, all compounds in the group are strongly reactive.

Potential Risks Because of Reactivity

<u>Reactions with Oxygen (air)</u>

$R_3Al + O_2 \rightarrow Al_2O_3 + H_2O + CO_2$

$R_2AlCl + O_2 \rightarrow Al_2O_3 + H_2O + CO_2 + HCl + heat$

The above reactions are vigorous and will generally cause the material to ignite resulting in a fire that is difficult to extinguish. Often, the recommended fire fighting practice is simply to let the material burn itself to extinction.

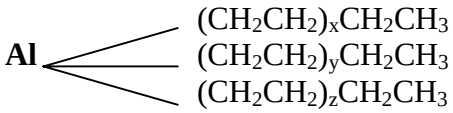
Reactions with Water

$R_3Al + H_2O \rightarrow Al(OH)_3 + RH + heat$
$R_2AlH + H_2O \rightarrow Al(OH)_3 + H_2 + heat$
$R_2AlCl + H_2O \rightarrow Al(OH)_3 + RH + HCl + heat$

The above reactions are even more violent than those with oxygen. The reaction with water creates flammable gases that are easily ignited by the fire already created by the organoaluminum compound with water. For this reason, water is generally not recommended for use in fighting aluminum alkyl fires. It can be concluded that exposure of aluminum alkyls to test animals would be cruel and not generate meaningful data. In fact, the use of any test method where water is not excluded is of no value.

Hazard Characterization
Because of the strong reactivity of the aluminum alkyls, these compounds are expected to cause thermal burns to eye and skin and inhalation may cause metal fume fever (Occupational Medicine, 1993). These chemicals are required to be labeled as spontaneously combustible, water reactive and flammable.

C2 - C20 Complexes
This group of sponsored materials includes the mixture, Aluminum, tri C2 -C20 alkyl complexes (CAS No. 68908-97-4) as well as the compounds in this mixture as shown in Table 3. The separate compounds are included because of the way these materials are designated for USEPA Toxic Substances Control Act (TSCA) purposes, however only the mixture is actually produced commercially. This mixture is composed of the species described by the structure shown below:



where x, y and z are integers from 0 - 16 corresponding to a Poisson distribution. This mixture is mostly composed of the C6 - C14 alkyls. It is never isolated into its individual components and is used on-site by chemical companies but not sold. Thus, we have considered the mixture, for classification purposes, as a single entity.

Conclusion
Table 1 demonstrates the similar structures of the aluminum alkyls. Table 2 provides information on the similarity of physical chemical properties. Although the sizes of the molecules are distinctly different from each other, their unique reactivity with both water and air shows reactions that preclude testing of these compounds. For example, because of the reactive properties, such compounds cannot be mixed in ordinary diets or administered in water. They are so reactive there is no possibility of administering repeated doses to animals because the acute hazards will prevent study of meaningful sub-chronic effects; the effect on tissues from single exposures obviates meaningful testing from repeated insults. Decomposition, which occurs almost spontaneously in air or water, precludes testing a moiety that resembles the parent material. In addition, decomposition products are substantially different enough from the parent materials to disallow any meaningful association with the parent chemical. Some decomposition products are shown in the reactivity section and exhibit corrosive effects as well as explosive potential.

Information from OSHA and ACGIH suggests that there are substantial hazards presented to technicians in the laboratory that would preclude testing these materials in a manner safe to humans. Finally, acute hazards to these materials (e.g. thermal burns to the eyes, skin, respiratory tract, and gastrointestinal tract) are such as to prevent testing them humanely, and without substantial pain and suffering to the species exposed.

The inclusion of these aluminum alkyls in the same category is based on the very similar structures shown in Table 1. However, the most compelling evidence of likely similar mechanisms of action is demonstrated in Table 2. Some of the characteristics of these alkyls are compared in Tables 2a and 2b. In appearance, all are colorless liquids except the dichloride compound (a solid) and the aluminum trialkyls (C2-C20), which are milky in color. All react violently with both water and air. Vapor pressures, although they cannot be directly compared, would all be expected to be below one mm Hg at 25^{o}C. Flash points are all very low. Comparable properties are shown in Tables 2a and 2b.

References

Mole J. and Jeffery, E.A., "Organoaluminum Compounds", Elsevier Publishing Company. Amsterdam 1972.
Wissink, H.G., *Aluminum alkyl reactivity.* Chemical & Engineering News. 1997. **75**, 9.

Occupational Safety and Health Administration, OSHA. 1988. Final Rule on Air Contaminants Project. 54FR2324 et seq.

Albemarle. August, 2000. Product Stewardship Manual. Aluminum Alkyls.

Tajima and Marsel as cited in Mole and Jeffery, 1972.

Smith and Wartik as cited in Mole and Jeffery, 1972.

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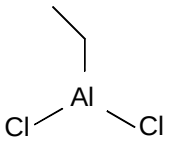
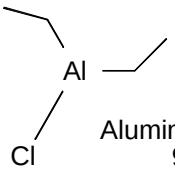
Occupational Medicine: State of the Arts Reviews, **8.** No. 3, 1993.

TABLE 1



Aluminum dichloroethyl
563-43-9



Aluminum chlorodiethyl
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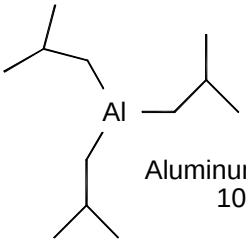
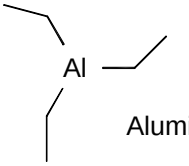


Aluminum tri isobutyl
100-99-2



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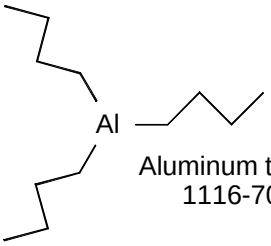
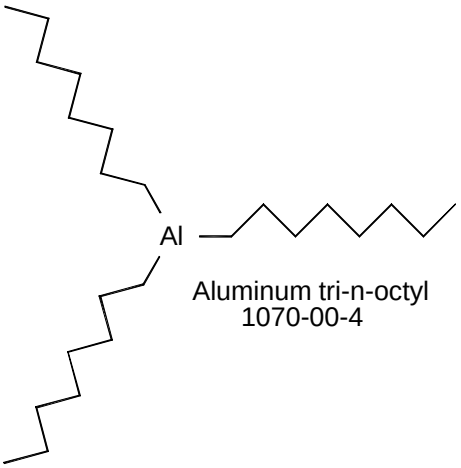
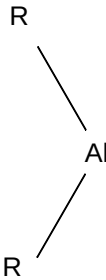
97-93-8



Aluminum tributyl
1116-70-7

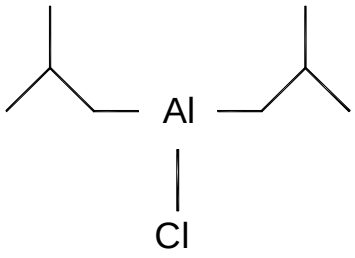


Aluminum tri-n-octyl
1070-00-4

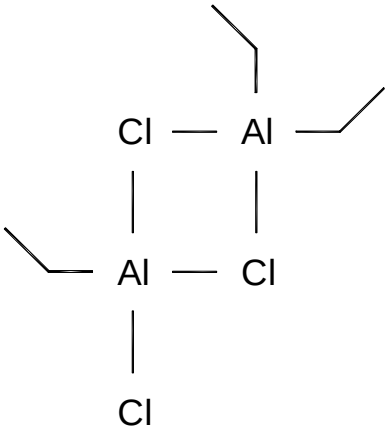


Aluminum tri C2-C20 alkyl complexes
68908-97-4

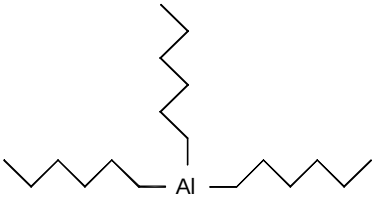
where R = C2 - 20



Aluminum chlorobis (2-methylpropyl)
1779-25-5



Aluminum, di-m-chlorochlorotriethyldi-
12075-68-2



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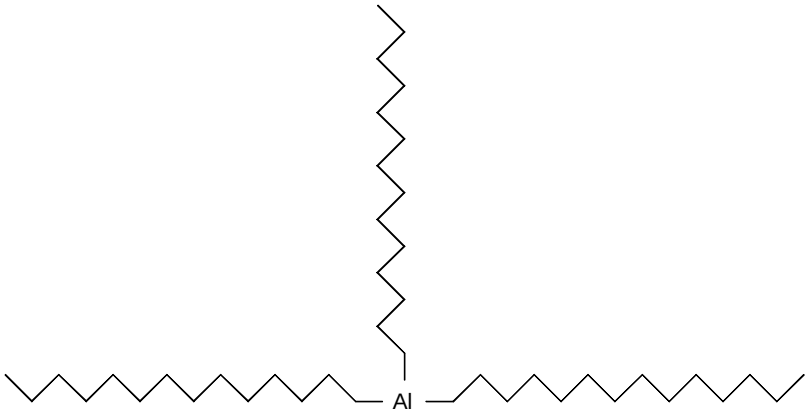
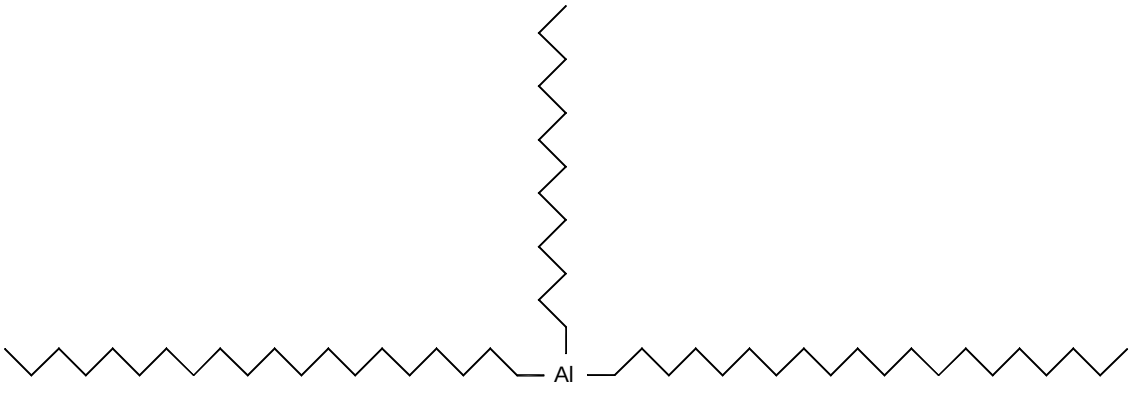


Aluminum tritetradecyl
1529-58-4



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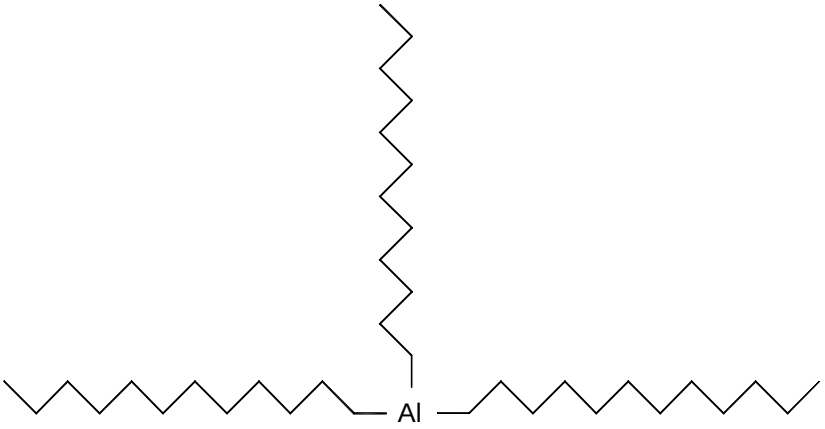

Aluminum tridodecyl
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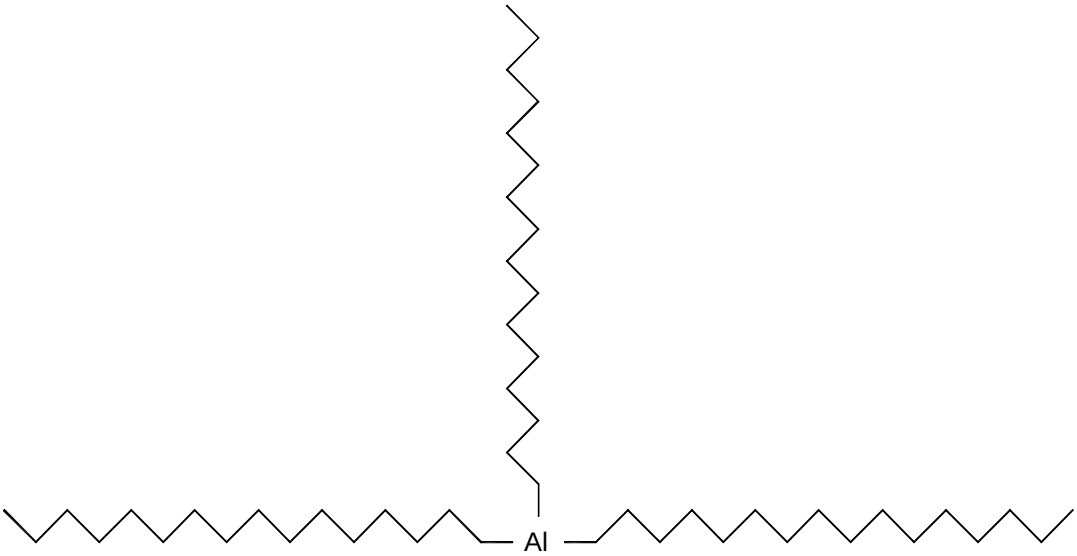

Aluminum trihexadecyl
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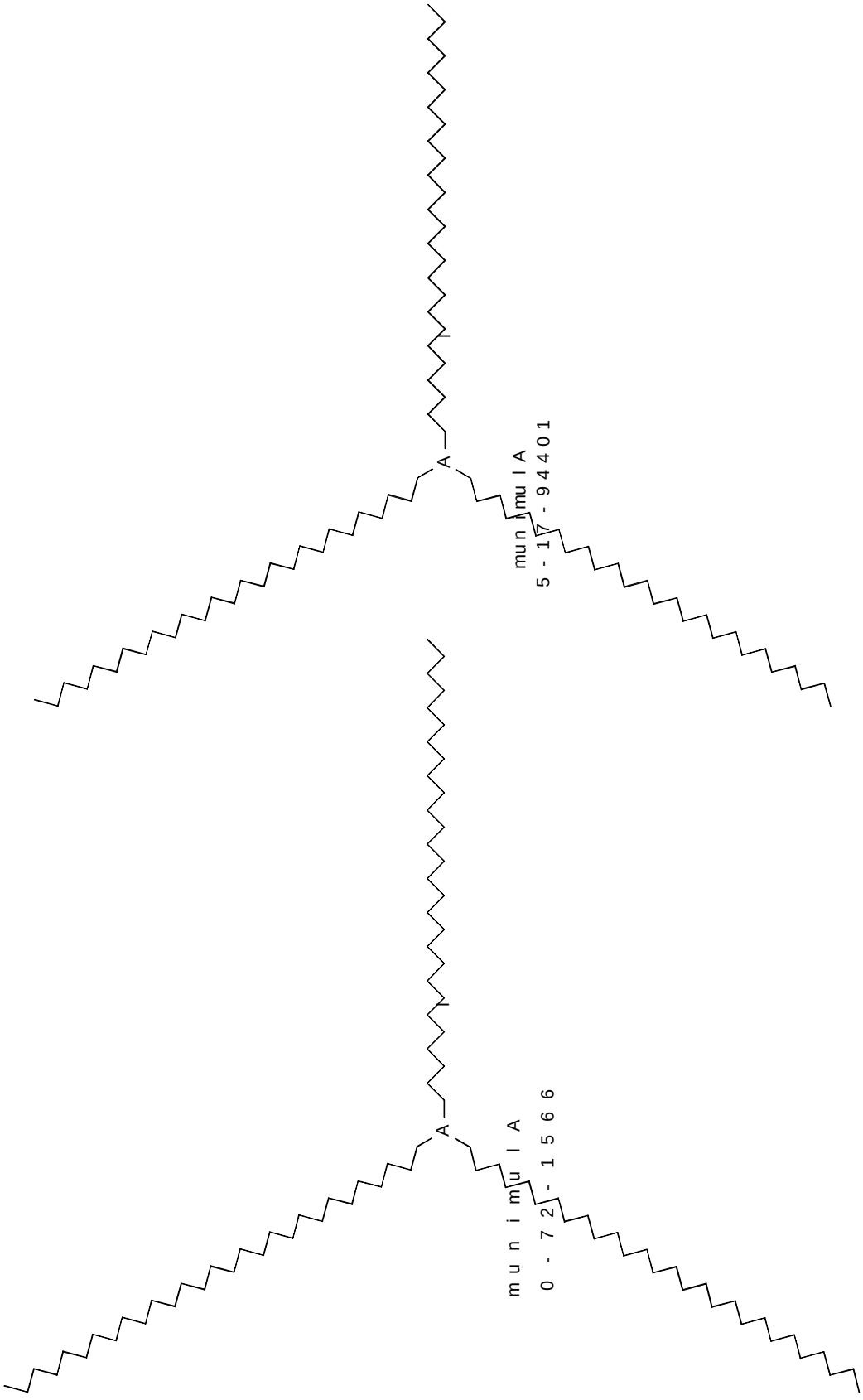
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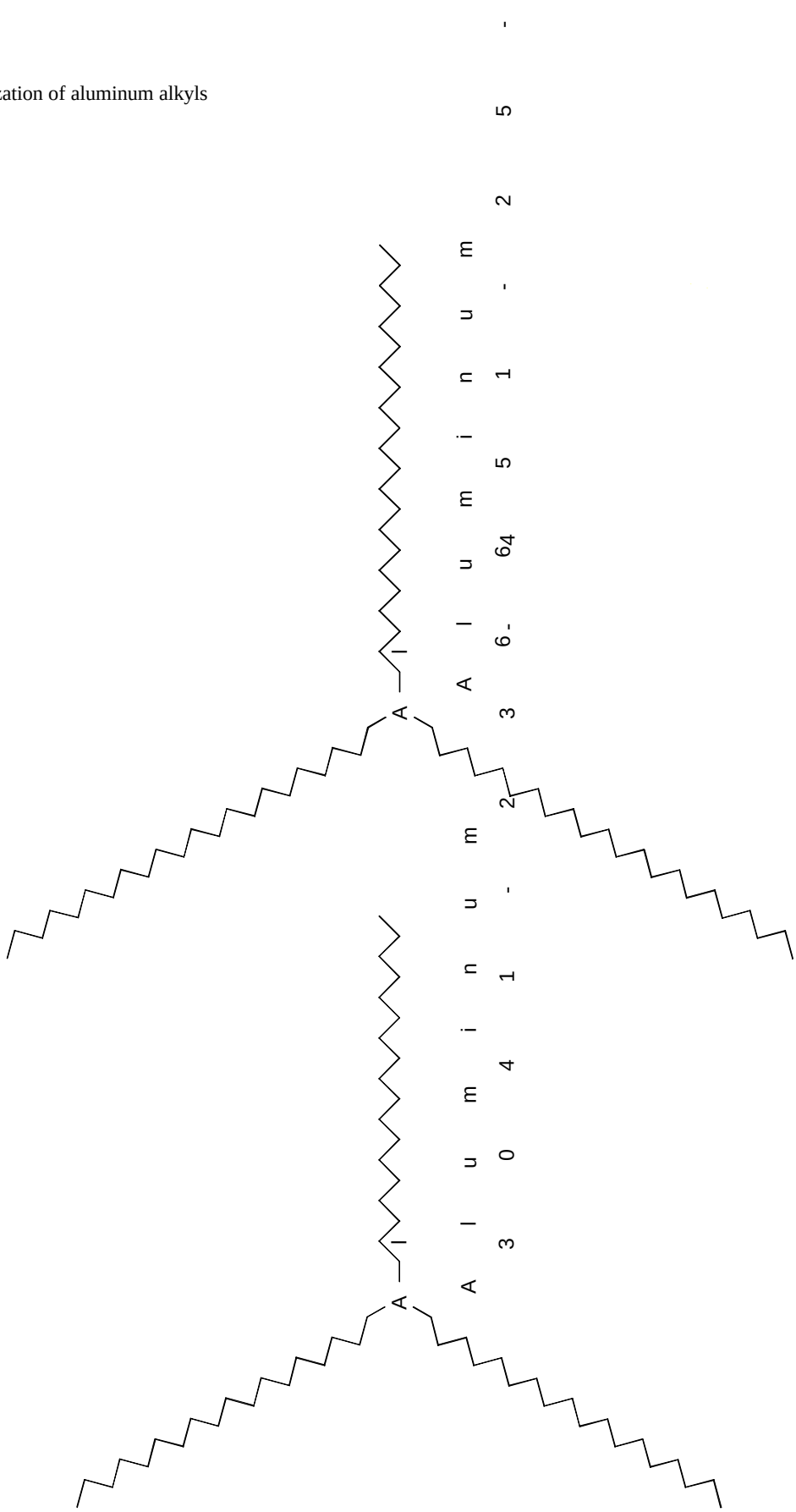
munimulA
0-72-1566


Aluminum-36-Aluminum-25-Aluminum-14-Aluminum-03-Aluminum-12

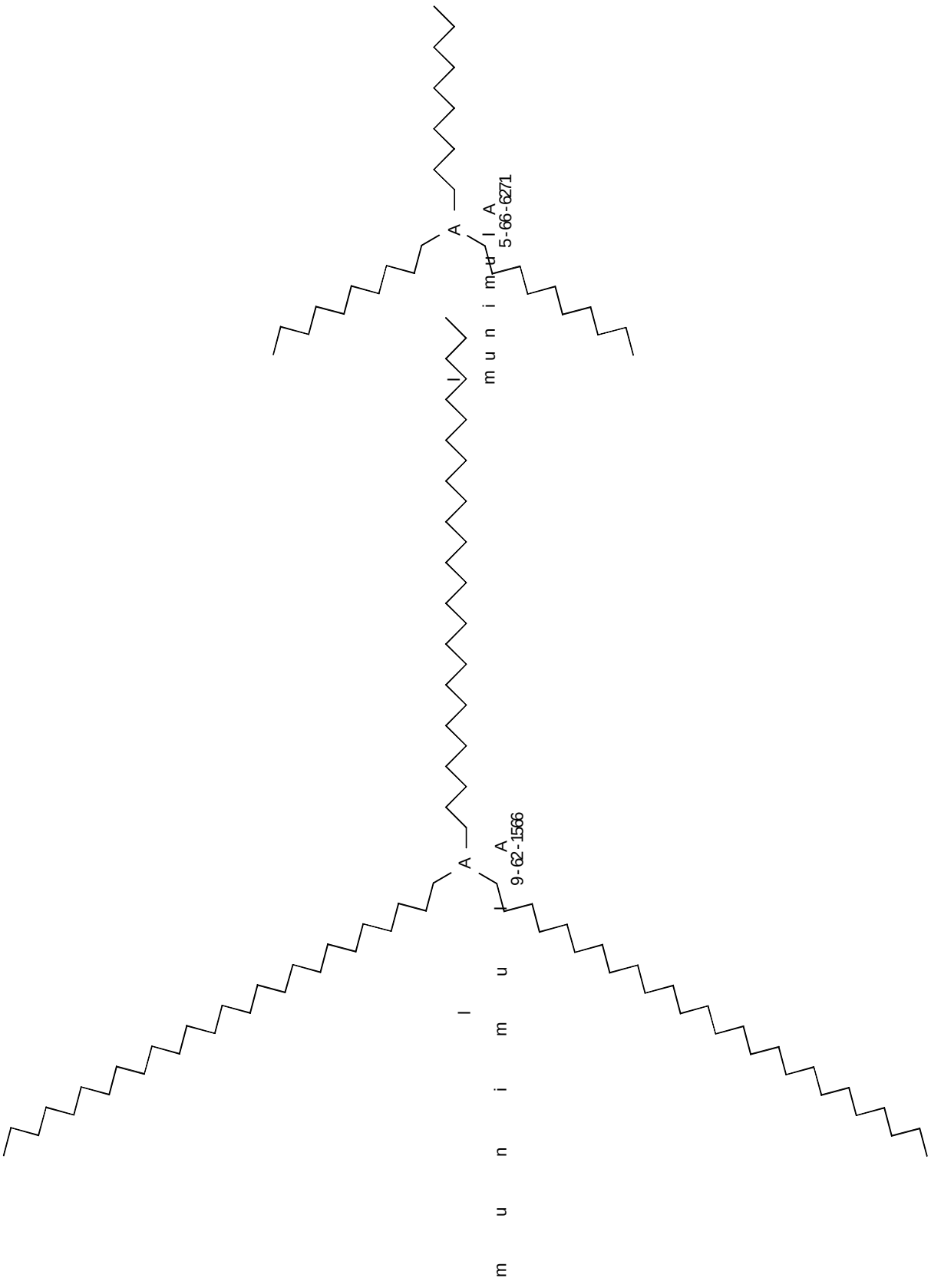

Aluminum
Aluminum
Aluminum
A
A
A
9-62-1566
5-66-6271

Table 2
Physical/Chemical Properties
Aluminum Alkyls

Values are for materials as sold or shipped

Chemical	CAS	Molecular Formula	Molecular Weight	Melting Point °C	Boiling Point °C @ mm Hg*	Density g/ml/ °C	Vapor Pressure mm Hg/°C	Flash Point °C	Appearance	Solubility
aluminum triethyl	97-93-8	$(C_2H_5)_3Al$	114.2	-52 (e)	185@760 (b)	0.83 @25 (b, e)	0.025/25 (b)	ignites spontaneously	colorless liquid	violent reaction w/water
aluminum chlorodiethyl	96-10-6	$(C_2H_5)_2AlCl$	120.6	-85 (e)	214@760 (b)	0.96@25 (b, e)	0.17/25 (b)	-23 (b)	colorless liquid	violent reaction w/water
aluminum tri isobutyl	100-99-2	$(iC_4H_9)_3Al$	198.3	6 (f)	214@760 (b)	0.78@25 (b)	0.133/251/47 (b, f)	-23 (b)	colorless liquid	violent reaction w/water
aluminum dichloroethyl	563-43-9	$C_2H_5AlCl_2$	126.9	32 (b)	203@760 (b)	1.2@25 (b)	10/80 (b)	ignites spontaneously	white crystalline solid	violent reaction w/water
aluminum tri n-octyl 7% solvent	1070-00-4	$(nC_8H_{17})_3Al$	366.7	ND	361@760 (b)	0.83@25 (b)	10^{-7}/40 (b)	ignites spontaneously	colorless liquid	violent reaction w/water
aluminum tributyl	1116-70-7	$(nC_4H_9)_3Al$	198.3	ND	240@760 (b)	0.82@25 (b)	<0.75/80 (b)	ignites spontaneously	colorless liquid	violent reaction w/water
aluminum trihexyl	1116-73-0	$(nC_6H_{13})_3Al$	282.5	-60 -77 (b, e)	ND	0.65@25 0.8@30 (b, e)	<0.75/80 (f)	ignites spontaneously	colorless liquid	violent reaction w/water
aluminum tri C_2-C_{20} alkyls	68908-97-4	ND	ND	ND	ND	ND	ND	ND	milky colored liquid	violent reaction w/water

(a) Mole and Jeffery 1972
(b) Albemarle (2000)
(d) CONDEA
(e) AKZO Nobel(c) Amoco (2000)
(f) Crompton (formerly Witco)

Table 2 Cont.

Values are for materials as sold or shipped

Chemical	CAS	Molecular Formula	Molecular Weight	Melting Point °C	Boiling Point °C/ mm Hg	Density g/ml/ °C	Vapor Pressure mm Hg/°C	Flash Point °C	Appearance	Solubility
aluminum trichloro triethyldi	12075-68-2	$(C_2H_5)_3Al_2Cl_3$	248	Decomposes before measurement (f)			8.27/80 (f)	Ignites spontaneously	liquid	violent reaction with water
Aluminum diisobutyl chloride	1779-25-5	$(C_4H_9)_2AlCl$	176	Decomposes before measurement (f)			0.22/80 (f)	Ignites spontaneously	liquid	violent reaction with water

(a) Mole and Jeffery 1972
(b) Albemarle (2000)
(c) Amoco (2000)
(d) CONDEA
(e) AKZO Nobel
(f) Crompton (formerly Witco)

Table 2a
Comparison of Physical Appearance
and
Reactions with Water

Chemical	CAS	Appearance	Solubility
aluminum triethyl	97-93-8	Colorless liquid	Violent reaction w/water
aluminum chlorodiethyl	96-10-6	Colorless liquid	Violent reaction w/water
aluminum tri isobutyl	100-99-2	Colorless liquid	Violent reaction w/water
aluminum dichloroethyl	563-43-9	White crystalline solid	Violent reaction w/water
aluminum tri n-octyl 7% solvent	1070-00-4	Colorless liquid	Violent reaction w/water
aluminum tributyl	1116-70-7	Colorless liquid	Violent reaction w/water
aluminum trihexyl	1116-73-0	Colorless liquid	Violent reaction w/water
aluminum trichloro triethyldi	12075-68-2	Liquid	Violent reaction w/water
aluminum diisobutyl chloride	1779-25-5	Liquid	Violent reaction w/water
aluminum tri C2-C20 alkyls	68908-97-4	Milky colored liquid	Violent reaction w/water

Table 2b
Comparison of Flash Points for Aluminum Alkyls

Chemical	CAS	Flash Point ^{o}C
Aluminum triethyl	97-93-8	Ignites spontaneously
Aluminum chlorodiethyl	96-10-6	-23
Aluminum tri isobutyl	100-99-2	-23
Aluminum dichloroethyl	563-43-9	Ignites spontaneously
Aluminum tri n-octyl 7% solvent	1070-00-4	Ignites spontaneously
Aluminum tributyl	1116-70-7	Ignites spontaneously
Aluminum trihexyl	1116-73-0	Ignites spontaneously
Aluminum trichloro triethyldi	12075-68-2	Ignites spontaneously
Aluminum diisobutyl chloride	1779-25-5	Ignites spontaneously
Aluminum tri C_2-C_{20} alkyls	68908-97-4	<38